

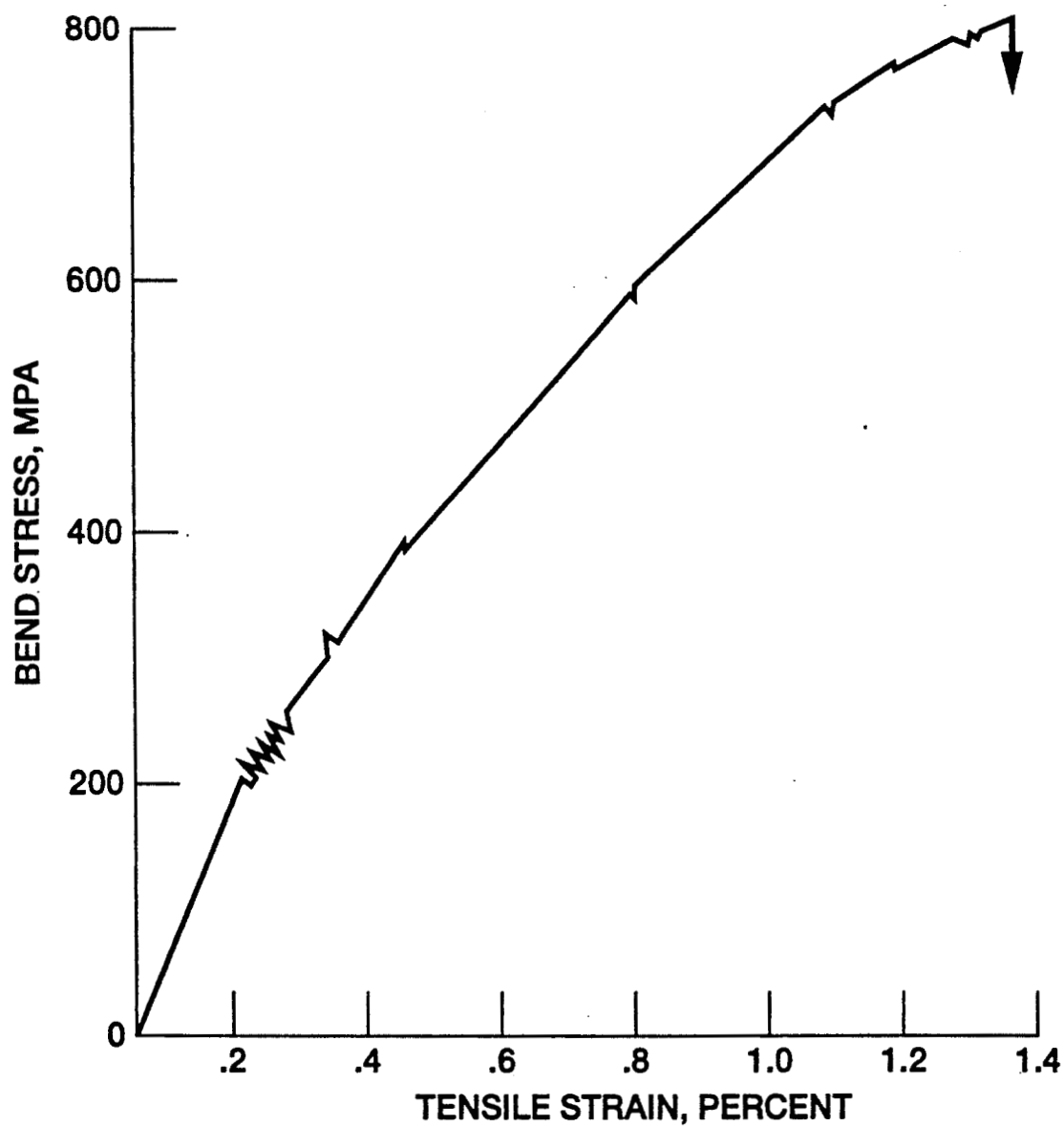


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United States Patent [19][11] **Patent Number:** **5,214,004****Bansal**[45] **Date of Patent:** **May 25, 1993**[54] **CERAMIC FIBER REINFORCED
GLASS-CERAMIC MATRIX COMPOSITE**[75] **Inventor:** **Narottam P. Bansal**, No. Olmsted,
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represented by the Administrator of
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Administration**, Washington, D.C.[21] **Appl. No.:** **892,055**[22] **Filed:** **Jun. 4, 1992**[51] **Int. Cl.⁵** **C03C 10/06; C03C 14/00**[52] **U.S. Cl.** **501/8; 501/32;
501/89; 501/95; 428/428; 428/698; 264/58**[58] **Field of Search** **501/8, 17, 32, 95, 89,
501/69; 264/58; 428/428, 698**[56] **References Cited****U.S. PATENT DOCUMENTS**4,410,635 6/1983 Brennan et al. 501/88
4,464,475 8/1984 Beall et al. 501/94,588,699 5/1986 Brennan et al. 501/9
4,615,987 10/1986 Chyung et al. 501/8
4,626,515 12/1986 Chyung et al. 501/32
4,634,683 1/1987 Dumbaugh et al. 501/32
4,666,869 5/1987 Dumbaugh, Jr. 501/32
4,919,991 4/1990 Gadkaree 428/113
4,992,318 2/1991 Gadkaree 501/95 X
5,164,341 11/1992 Chyung et al. 501/95 X*Primary Examiner*—Karl Group*Attorney, Agent, or Firm*—Gene E. Shook; Guy M.
Miller; James A. Mackin[57] **ABSTRACT**

A slurry of BSAS glass powders is cast into tapes which are cut to predetermined sizes. Mats of continuous CVD-SiC fibers are alternately stacked with these matrix tapes. This tape-mat stack is warm-pressed to produce a "green" composite which is heated to burn out organic constituents. The remaining interim material is then hot-pressed to form a BSAS glass-ceramic fiber-reinforced composite.

15 Claims, 1 Drawing Sheet



CERAMIC FIBER REINFORCED GLASS-CERAMIC MATRIX COMPOSITE

ORIGIN OF THE INVENTION

The invention described herein was made by an employee of the U.S. Government and may be manufactured or used by or for the Government without the payment of any royalties thereon or therefor.

TECHNICAL FIELD

This invention is concerned with a ceramic fiber-reinforced glass-ceramic matrix composite. The invention is particularly concerned with a high strength ceramic fiber reinforced composite which is refractory, strong, and tough for applications as high temperature structural materials.

It has been suggested that lithium aluminosilicate, magnesium aluminosilicate (cordierite), and calcium aluminosilicate glass ceramics reinforced with SiC fibers derived from polymers be used for such applications. Commercially available SiC fibers, known as Nicalon, have been satisfactory. However, the potential use of such prior art materials is limited to somewhat low temperatures of about 1000° C. to 1100° C.

It is, therefore, an object of the present invention to provide a new composite material having superior mechanical properties at high temperatures.

Another object of the invention is to provide a method of making a ceramic fiber-reinforced glass-ceramic matrix composite material for use in gas turbine and diesel engines.

BACKGROUND ART

Brennan et al U.S. Pat. No. 4,410,635 discloses silicon carbide fiber reinforced composites which include barium aluminosilicates. Chyung et al U.S. Pat. No. 4,615,987 describes silicon carbide fiber reinforced aluminosilicate glass-ceramics which include barium oxide and strontium oxide. These may be used at temperature ranges of 1000° C.-1300° C.

Brennan et al U.S. Pat. No. 4,588,699 is directed to a high strength magnesium aluminosilicate glass-ceramic matrix with silicon carbide fibers and including barium oxide. The matrix may be operated at temperatures at 1200° C.-1500° C. Dumbaugh, Jr. U.S. Pat. Nos. 4,634,683 and 4,666,869 disclose barium and/or strontium oxide aluminosilicate glasses.

Beali et al U.S. Pat. No. 4,464,475 described a glass-ceramic article containing osulmite (barium oxide) and which is capable of being used at temperatures of 1300° C. and higher. The bodies may be used as a matrix for fiber reinforced structures. Gadkaree U.S. Pat. No. 4,919,991 is directed to a ceramic matrix composite on silicon fiber yarns.

DISCLOSURE OF THE INVENTION

The objects of the invention are achieved with a fiber-reinforced composite which is composed of a $(1-x)\text{BaO} \cdot x\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (BSAS) glass ceramic matrix where $x=0.05$ to 1. The matrix has been reinforced with CVD SiC continuous fibers. The method of assembly includes preparing a slurry of BSAS glass powders and casting this slurry into tapes. After the tapes are dried they are cut to the proper size.

Continuous CVD-SiC fibers are formed into mats of the desired size. The matrix tapes and the fiber mats are alternately stacked in the proper orientation. This tape-

mat stack is warm pressed to produce a "green" composite.

The "green" composite is then heated to an elevated temperature to burn out organic constituents. The remaining interim material is then hot pressed to form a BSAS glass-ceramic fiber-reinforced composite which may be machined to size.

DESCRIPTION OF THE DRAWING

The objects, advantages and novel features of the invention will be more fully apparent from the following detailed description when read in conjunction with the accompanying drawing which is a graph showing the three point flexural stress-strain behavior for a 24 fiber volume percent silicon carbide fiber/BSAS ($x=1$) glass-ceramic composite material at room temperature.

BEST MODE FOR CARRYING OUT THE INVENTION

The composite of the present invention is produced by a tape method in which an aqueous slurry of glass powder along with a fugitive organic binder, plasticizer, glycerine, and surfactant is prepared. Glass powders having an average particle size of about 1.5 μm have been satisfactory. A binder identified as Methocel 20-214 which is a commercially available material from the Dow Chemical Company has been suitable. A plasticizer known commercially as Polyglycol E-400 from the Dow Chemical Company has been adequate. A surfactant material sold commercially as Tritonex 100 has provided satisfactory results.

This slurry is first ball milled and then cast into tapes. This may be facilitated by using a doctor blade. After the tape has dried, it is cut to size.

Continuous CVD SiC fibers that were supplied by Textron Specialty Materials are wound onto a drum. Commercially available adhesive tape is used to hold the fibers in their proper position on the drum. The fibers are then cut into unidirectional mats of desired predetermined size whose fiber orientation and integrity are maintained by the adhesive tape.

The required number of matrix tapes and fiber mats are alternately stacked in a desired orientation in a warm press die. After stacking, this material is warm pressed to produce a "green" composite.

The "green" composite is then removed from the warm press die and wrapped in either graphite foil or molybdenum foil. The wrapped "green" composite is loaded into a hot pressing die where it is heated to an elevated temperature between about 400° C. to 500° C. to burn out organic constituents to produce an interim material.

The interim material is then hot pressed under vacuum using temperatures of 1250° C.-1500° C., a pressure of 2 to 4 KSI, and a time of 15 to 120 minutes. After cooling to room temperature and pressures, the resulting composites are then removed from the die.

A number of the composites were cut into test bars for flexural strength measurements and other characterizations. Referring to the drawing there is shown a graph of the 3-point flexural stress-strain behavior for a 24 volume percent SiC fiber/BSAS ($x=1$) glass-ceramic matrix composite material. The flexural stress-strain line is for room temperature measurements. Unidirectional SiC fiber/BSAS ($x=1$) glass-ceramic matrix composites having room temperature 3-point flexural

stress of greater than 1000 MPA have been fabricated with 27 volume percent fiber loading.

While the preferred embodiment of the invention has been shown and described, it will be appreciated that various modifications may be made to the invention without departing from the spirit thereof or the scope of the subjoined claims. This silicon carbide fiber-reinforced BSAS glass-ceramic matrix composite is a new and improved structural material. The composite fabricated by the aforementioned method has mechanical properties superior to existing materials and a potential for use at temperatures as high as 1450° C. to 1500° C.

What is claimed is:

1. A method of producing a ceramic fiber-reinforced glass-ceramic matrix composite comprising the steps of preparing an aqueous slurry of $(1-x)$ BaO - x SrO - Al_2O_3 - $2SiO_2$ ($x=0.05$ to 1) (BSAS) glass powder, an organic binder, a plasticizer, glycerine, and a surfactant, ball milling said slurry, casting said slurry into tape thereby forming a glass-matrix tape, drying said glass matrix tape, cutting said glass matrix tape, winding continuous chemical vapor deposition (CVD) SiC fibers onto a drum, cutting said fibers on said drum thereby forming a fiber mat, alternating a plurality of said glass matrix tapes with a plurality of said fiber mats thereby forming a tape-mat stack, warm pressing said tape-mat stack thereby forming a "green" composite, wrapping said "green" composite in foil, heating said wrapped "green" composite whereby organic constituents are burned out thereby forming an interim material, and hot pressing said interim material to produce a silicon carbide fiber-reinforced (BSAS) glass-ceramic matrix composite.
2. A method as claimed in claim 1 wherein the (BSAS) glass powder has an average particle size of about 2.5 μ m.
3. A method as claimed in claim 1 wherein the plasticizer in the slurry is polyglycol.
4. A method as claimed in claim 1 wherein the organic constituents are burned out at about 400° C. to about 500° C.

5. A method as claimed in claim 1 wherein the SiC fiber comprises about 24 volume percent of the composite.

6. A method as claimed in claim 1 wherein the "green" composite is wrapped in graphite foil.

7. A method as claimed in claim 1 wherein the "green" composite is wrapped in molybdenum foil.

8. A method as claimed in claim 1 wherein said "green" composite is hot pressed at a temperature between about 1250° C. and about 1500° C.

9. A method as claimed in claim 8 wherein the hot pressing occurs at a pressure between about 2 KSI and about 4 KSI.

10. A method as claimed in claim 9 wherein said hot pressing occurs at a time between about 15 minutes and about 120 minutes.

11. In a method of forming a silicon carbide fiber-reinforced glass-ceramic matrix composite the steps of alternating a glass-matrix tape composed of $(1-x)$ BaO - x SrO - Al_2O_3 - $2SiO_2$ ($x=0.05$ to 1), organic binder, plasticizer, glycerine, and surfactant, with a fiber mat comprising about 20 percent to about 40 percent by volume of silicon carbide fibers thereby forming a tape-mat stack,

warm pressing said stack thereby forming a "green" composite,

heating said "green" composite thereby burning out organic material therefrom,

hot pressing the resulting material at a temperature of about 1250° C. to about 1500° C. for about 15 minutes to about 120 minutes at a pressure of about 2 KSI to about 4 KSI thereby producing a silicon carbide fiber-reinforced glass-ceramic matrix composite, and

cooling said composite to room temperature.

12. A method as claimed in claim 11 wherein the plasticizer is polyglycol.

13. A method as claimed in claim 11 wherein the composite comprises about 24 volume percent SiC fibers.

14. A silicon carbide fiber-reinforced glass-ceramic matrix composite for use at temperatures up to about 1500° C. comprising

about 20 to about 40 percent of silicon carbide fiber by volume percent, and

about 60 percent to about 80 percent of a glass-ceramic matrix by volume percent, said glass-ceramic matrix comprising $(1-x)$ BaO - x SrO - Al_2O_3 - $2SiO_2$ ($x=0.05$ to 1).

15. A composite as claimed in claim 14 wherein the silicon carbide fiber content is about 24 volume percent.

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